

DECLARATION

I, Chizuko IKEDA, declare that I reside at 5-50-301,
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That I am familiar with the English and Japanese
languages;

That I have prepared a translation of Japanese Patent
Application No. 2003-358542, "複合成形体及びその製造方法, MOLDED
COMPOSITE ARTICLE AND PROCESS FOR PRODUCING THE SAME"; said
translation thereof being attached hereto and made a part of
this declaration;

That to the best of my knowledge and belief, the attached
translation is accurate and fairly reflects the contents and
meaning of the foregoing Japanese language document.

I declare, under penalty of perjury under the laws of
the United States of America, that the foregoing is true and
correct.

Executed, on November 15, 2011.

A handwritten signature in cursive script, reading "Chizuko Ikeda", is written over a horizontal line.

Chizuko IKEDA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy
of the following application as filed with this Office.

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Applicant(s): Daicel-Degussa Ltd.

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[Document Name] Claims

[Claim 1]

A molded composite article in which a resin member comprising a polyamide-series resin and a resin member
5 comprising a thermoplastic polyurethane-series resin are directly joined with each other, wherein each of the polyamide-series resin and the thermoplastic polyurethane-series resin has a polyether segment.

[Claim 2]

10 A molded composite article according to Claim 1, wherein the polyamide-series resin comprises a polyamide elastomer having a polyoxyC₂₋₄alkylene segment as a soft segment.

[Claim 3]

15 A molded composite article according to Claim 1, wherein the thermoplastic polyurethane-series resin comprises a thermoplastic polyether urethane elastomer having a polyoxyC₂₋₄alkylene segment as a soft segment.

[Claim 4]

20 A molded composite article according to Claim 1, wherein the polyamide-series resin comprises a polyamide elastomer comprising a polyamide segment and a polyether segment, and the proportion (weight ratio) of the polyamide segment relative to the polyether segment is, the former/the
25 latter = 9/1 to 2.5/7.5.

[Claim 5]

A molded composite article according to Claim 1,

wherein the proportion of the polyether segment in the polyamide-series resin constituting the resin member is 10 to 90% by weight relative to the whole resin, and the proportion of the polyether segment in the thermoplastic
5 polyurethane-series resin constituting the resin member is 10 to 90% by weight relative to the whole resin.

[Claim 6]

A molded composite article according to Claim 1, which is a shoe member or a roll member.

10 [Claim 7]

A process for producing a molded composite article recited in claim 1, which comprises

heating at least one resin selected from the group consisting of the polyamide-series resin and the
15 thermoplastic polyurethane-series resin recited in Claim 1, and

joining the both resins with each other.

[Claim 8]

A process according to Claim 7, wherein the
20 polyamide-series resin and the thermoplastic polyurethane-series resin are joined with each other in the molding process by a molding method selected from the group consisting of a thermoforming, an injection molding, an extrusion molding, and a blow molding.

[Document Name] Description

[Title of the Invention] MOLDED COMPOSITE ARTICLE AND
PROCESS FOR PRODUCING THE SAME

[Technical Field]

5 [0001]

The present invention relates to a molded composite
article (or composite molded article) in which a resin member
comprising a polyamide-series resin having a polyether
segment is joined to a resin member comprising a
10 thermoplastic polyurethane-series resin having a polyether
segment in a one-piece construction without an adhesive,
and a process for producing the same.

[Background Art]

[0002]

15 In order to improve design or decorative property,
or in order to impart excellent touch or texture (e.g.,
soft texture), there have been proposed composites (molded
composite articles) formed with a combination of a plurality
of resins each having a different hardness, for example,
20 a molded composite article in which at least a part of a
resin molded article is coated with a thermoplastic
elastomer. Such a molded composite article is usually
produced by adhesion of a plurality of molded members through
an adhesive. For example, Patent Document 1 discloses a
25 resin molded article in which a plurality of resin molded
articles formed with a polyamide resin or others are weld
or adhered to each other through a finishing agent such

as a urethane polymer or a urethane-series adhesive.
However, such a process using an adhesive is not only
uneconomical due to complicated steps, but also has problems
such as environmental pollution by an organic solvent or
5 others.

[0003]

On the other hand, from the viewpoint of
rationalization of production processes or environmental
protection, a process for thermal fusing of a plurality
10 of molded members has been adopted. The molded composite
article obtained by thermal fusing is usually manufactured
by a molding process such as a two-color (or double) molding
or an insert molding. However, combination of materials
which are different in species and are acceptable for thermal
15 fusing is significantly limited. Moreover, it is not easy
to establish molding conditions for obtaining enough bonded
strength. Therefore, in order to reinforce the fused part,
such a method is utilized in addition to thermal fusing
or welding, that a method for preparing a concavo-convex
20 site (or part) in an area to be bonded of the molded member
for mechanical joining, a method for coating a primer or
others on an area to be bonded, or other methods. In such
a method, however, the molded composite article is
deteriorated in flexuous property. For example, the
25 hardened primer layer easily forms a crack with bending.
Moreover, the method tends to require a complicated
structure of the molded member, or increases the number

of production steps.

[0004]

In order to solve these problems, it has been investigated to use a thermoplastic polyurethane as a material for a resin member constituting a molded composite article. The thermoplastic polyurethane itself is relatively excellent in adhesiveness. For example, in a usage(or purpose) of shoe(s), a molded composite plastic article comprising a polyamide resin and a thermoplastic polyurethane is practically used as a shoe sole. Moreover, Patent Document 2 discloses that a lightened shoe sole is obtained by injection-molding a polyamide elastomer containing a foaming agent into a mold, with inserting or putting a molded article of a thermoplastic resin such as a polyether amide, a polyether ester or a polyurethane in a mold, and adhering to the thermoplastic resin molded article (un-lightweight (un-lightened) plastic) and the elastomer (lightweight thermoplastic elastomer). Patent Document 3 discloses a molded composite article in which a rigid plastic molded member formed of a blended matter of a polypropylene and a polyamide is coated with a non-rigid (or flexible) plastic containing a thermoplastic polyurethane and a plasticizer by thermal fusing. However, even in such a molded composite article (for example, a molded composite article using a polyurethane resin), the adhesive strength between two materials (e.g., an adhesive strength relative to a polyamide elastomer as a counterpart

member) has not been enough yet. Therefore, such a composite is affected by not only conditions for molding or conditions of materials to be used (e.g., production lot) but also using environment of the product (molded composite article),
5 resulting in unstableness of the bonded strength or the duration of the molded composite article (particularly the duration of the adhered site).

[Patent Document 1] JP-8-267585A (Claims)

[Patent Document 2] JP-8-50533A (Claims)

10 [Patent Document 3] JP-7-125155A (Claims)

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0005]

It is therefore an object of the present invention
15 to provide a molded composite article in which, even using a polyamide-series resin member and a thermoplastic polyurethane-series resin member different in character from each other, the both members are directly and firmly joined together without an adhesive; and a process for
20 producing the same.

[0006]

It is another object of the present invention to provide a process for producing a molded composite article in which a polyamide-series resin member and a thermoplastic
25 polyurethane-series resin member are firmly joined together by thermal fusing in a convenient manner without going through complicated production steps.

[Means to Solve the Problems]

[0007]

The inventors of the present invention made intensive studies to achieve the above objects and finally found that
5 the combination of a polyamide-series resin and a thermoplastic polyurethane-series resin both of which have a polyether segment achieves firm joining or bonding of both resin members due to enhancement of affinity between both resins. The present invention was accomplished based
10 on the above findings.

[0008]

That is, the molded composite article of the present invention is a molded composite article in which a resin member comprising a polyamide-series resin and a resin
15 member comprising a thermoplastic polyurethane-series resin are directly joined with each other, wherein each of the polyamide-series resin and the thermoplastic polyurethane-series resin has a polyether segment. The polyamide-series resin may comprise a polyamide elastomer
20 having a polyoxyC₂₋₄alkylene segment as a soft segment. Moreover, the thermoplastic polyurethane-series resin may comprise a thermoplastic polyether urethane elastomer having a polyoxyC₂₋₄alkylene segment as a soft segment. Moreover, at least one member out of the polyamide-series
25 resin and the thermoplastic polyurethane-series resin may comprise at least a polytetramethylene glycol unit (a polytetramethylene ether unit). The polyamide-series

resin may comprise a polyamide elastomer comprising a polyamide segment and a polyether segment, and the proportion (weight ratio) of the polyamide segment relative to the polyether segment may be, the former/the latter =
5 about 9/1 to 2.5/7.5. The proportion of the polyether segment in the polyamide-series resin constituting the resin member may be about 10 to 90% by weight relative to the whole resin, and the proportion of the polyether segment in the thermoplastic polyurethane-series resin
10 constituting the resin member may be about 10 to 90% by weight relative to the whole resin.

[0009]

The molded composite article of the present invention is suitable for a component member of a shoe or a roll.

15 [0010]

Such a molded composite article may be produced by heating at least one resin selected from the group consisting of the polyamide-series resin and the thermoplastic polyurethane-series resin, and joining the polyamide resin
20 and the thermoplastic polyurethane-series resin with each other. For example, the joining may be conducted either by heating the thermoplastic polyurethane-series resin to be molten, and bringing the thermoplastic polyurethane-series resin in the molten state into contact
25 with a part of a resin member comprising the polyamide-series resin, or by heating the polyamide-series resin to be molten, and bringing the polyamide-series resin in the molten state

into contact with a part of a resin member comprising the thermoplastic polyurethane-series resin. Furthermore, the joining may be conducted by heating each of the polyamide-series resin and the thermoplastic

5 polyurethane-series resin, and bringing the thermoplastic polyurethane-series resin in the molten state into contact with the polyamide-series resin in the molten state.

Moreover, the polyamide-series resin and the thermoplastic polyurethane-series resin may be joined with each other
10 in the molding process by a molding method selected from the group consisting of a thermoforming, an injection molding, an extrusion molding, and a blow molding.

[0011]

Incidentally, throughout this specification, the
15 meaning of the term "resin" includes "a resin composition". Moreover, throughout this specification, the term "adhesion (or adhering)" means a technique for compounding a plurality of members through an adhesive, the term "joining (or bonding)" means a technique for compounding a plurality
20 of members without an adhesive, and the both terms are distinguished from each other. Fusing (or thermal fusing) is one embodiment of joining.

[Effects of the Invention]

[0012]

25 According to the present invention, since the polyamide-series resin having a polyether segment is combined with the thermoplastic polyurethane-series resin

having a polyether segment, in spite of difference in properties between the polyamide-series resin and the thermoplastic polyurethane-series resin, by enhancing the affinity between the polyamide-series resin and the thermoplastic polyurethane-series resin, direct and strong bonding or joining of the polyamide-series resin member with the thermoplastic polyurethane-series resin member is achieved without an adhesive. Moreover, according to the process of the present invention, a molded composite article is producible in which a polyamide-series resin and a thermoplastic polyurethane resin member are firmly joined together by thermal fusing in a simple manner without going through complicated production steps.

[Preferred Embodiment of the Invention]

[0013]

[Molded composite article]

The molded composite article of the present invention comprises a resin member comprising a polyamide-series resin and a resin member comprising a thermoplastic polyurethane-series resin and directly joined with the polyamide-series resin member, and each of the polyamide-series resin and the thermoplastic polyurethane-series resin has a polyether segment.

[0014]

(Polyamide-series resin)

The polyamide-series resin comprises a polyamide-series resin having at least a polyether segment

[e.g., a polytetramethylene glycol (PTMG, polytetramethylene ether) segment or unit, a polyoxyC₂₋₄alkylene segment or unit such as a polyethylene glycol or a polypropylene glycol]. At least one member
5 selected from the group consisting of a polyamide-series resin and a thermoplastic polyurethane-series resin (particularly a polyamide-series resin) may have at least a PTMG unit.

[0015]

10 Such a polyamide-series resin may include a polyamide obtained by using a component having a polyether segment [e.g., a diamine having a polyoxyC₂₋₄alkylene unit, a dicarboxylic acid and an aminocarboxylic acid] as at least a part of components among the constitution component of
15 the polyamide (e.g., a diamine, a dicarboxylic acid, and an aminocarboxylic acid). Moreover, the polyamide-series resin having the polyether segment may include a polyamide block copolymer (that is, a polyamide elastomer having a polyether component as a soft segment) obtained by reaction
20 of a polyamide component (polyamide block or segment) having a reactive terminal group with a polyether component (polyether block or segment) having a terminal group reactive to the above reactive terminal group of the polyamide component.

25 [0016]

Such a polyamide elastomer may also include for example a polyamide obtained by reaction of a polyamide

component having a terminal carboxyl group with a polyether
component having a terminal amino group, a polyamide
obtained by reaction of a polyamide component having a
terminal amino group with a polyether component having a
5 terminal carboxyl group, a polyamide obtained by reaction
of a polyamide component having a terminal carboxyl group
with a polyether component having a terminal hydroxyl group,
and others.

[0017]

10 As the polyether component having a reactive terminal
group, there can be utilized a component having a terminal
amino group [e.g., a polyoxyC₂₋₄alkylenediamine (such as
polyoxyethylenediamine)], a component having a terminal
carboxyl group (e.g., a half ester of a dicarboxylic acid(s)
15 with a polyoxyC₂₋₄alkylene glycol), a component having a
terminal hydroxyl group, for example, a polyoxyC₂₋₄alkylene
glycol [e.g., a polyethylene glycol, a polypropylene glycol,
a polytetramethylene ether glycol, a block copolymer of
these polyoxyalkylene glycols (such as a
20 polyoxyethylene-polyoxypropylene block copolymer); and an
alkyleneoxide adduct of an aromatic diol (e.g., a bisphenol
A-C₂₋₄alkyleneoxide adduct)].

[0018]

The above polyamide component having a reactive
25 terminal group includes an aliphatic polyamide, an alicyclic
polyamide, an aromatic polyamide, and others, and various
homopolyamides and copolyamides can be used.

[0019]

Among the aliphatic polyamide, the homopolyamide may include a condensation product of an aliphatic diamine component (for example, a C₆₋₁₂alkylenediamine such as tetramethylenediamine, hexamethylenediamine, or dodecanediamine) with an aliphatic dicarboxylic acid component (e.g., a C₆₋₁₄alkylenedicarboxylic acid such as adipic acid, sebacic acid, or dodecanedioic acid) (for example, a polyamide 46, a polyamide 66, a polyamide 610, a polyamide 612, and a polyamide 1010), a homopolyamide of a lactam (e.g., a lactam having about 4 to 16 carbon atoms, such as ϵ -caprolactam or ω -laurolactam) or an aminocarboxylic acid (e.g., an aminocarboxylic acid having about 4 to 16 carbon atoms, such as ω -aminoundecanoic acid) (for example, a polyamide 6, a polyamide 11, and a polyamide 12); and others. Moreover, the copolyamide may include a copolyamide which can be obtained by copolymerization of a monomer component capable of constituting a polyamide, e.g., the aliphatic diamine components, the aliphatic dicarboxylic acid components, the lactams and the aminocarboxylic acids. Examples of the copolyamide may include a copolymer of 6-aminocaproic acid and 12-aminododecanoic acid; a copolymer of 6-aminocaproic acid, 12-aminododecanoic acid, hexamethylenediamine and adipic acid; a copolymer of hexamethylenediamine, adipic acid, hydrogenated dimer acid and 12-aminododecanoic acid; a polyamide 6/11, a polyamide 6/12, a polyamide 66/11, a

polyamide 66/12; and others.

[0020]

The alicyclic polyamide may include a homopolyamide or copolyamide having at least one component selected from the group consisting of at least an alicyclic diamine and an alicyclic dicarboxylic acid (e.g., a C₅-10cycloalkane-dicarboxylic acid such as cyclohexane-1,4-dicarboxylic acid or cyclohexane-1,3-dicarboxylic acid) as a constitutive component. For example, there may be used an alicyclic polyamide obtained by using an alicyclic diamine and/or an alicyclic dicarboxylic acid as at least one component among a diamine component and a dicarboxylic acid component each constituting a polyamide-series resin. As the diamine component and the dicarboxylic acid component, the above-mentioned aliphatic diamine(s) and/or aliphatic dicarboxylic acid(s) are preferably used in combination with the alicyclic diamine(s) and/or alicyclic dicarboxylic acid(s). Incidentally, such an alicyclic polyamide has a high transparency and is known as what is called transparent polyamide. Among the alicyclic polyamides, a condensation product (a homo- or copolyamide) of the aliphatic dicarboxylic acid with the alicyclic diamine is preferred.

[0021]

Examples of the alicyclic diamine may include a diaminoC₅-10cycloalkane such as diaminocyclohexane; a bis(aminoC₅-8cycloalkyl)C₁-3alkane such as

bis(4-aminocyclohexyl)methane,
bis(4-amino-3-methylcyclohexyl)methane, or
2,2-bis(4'-aminocyclohexyl)propane; and others.

[0022]

5 The aromatic polyamide may include a polyamide in
which at least one component selected from the aliphatic
diamine component and the aliphatic dicarboxylic acid
component comprises an aromatic component, for example,
a polyamide having an aromatic component in a diamine
10 component [for example, a condensation product of an
aromatic diamine (e.g., metaxylylenediamine) and an
aliphatic dicarboxylic acid, such as MXD-6], a polyamide
having an aromatic component in a dicarboxylic acid
component [e.g., a condensation product of an aliphatic
15 diamine (e.g., trimethylhexamethylenediamine) and an
aromatic dicarboxylic acid (e.g., terephthalic acid,
isophthalic acid)], and others.

[0023]

As the polyamide component, there may be used a
20 polyamide having a dimer acid as a dicarboxylic acid
component, a polyamide to which a branched chain structure
is introduced by using a small amount of a polyfunctional
polyamine and/or polycarboxylic acid component, a modified
polyamide (such as an N-alkoxymethylpolyamide), and others.

25 [0024]

Incidentally, as the polyamide component, there may
be used a perfect (fully) aromatic polyamide (e.g., Aramid)

(a polyamide in which both a diamine component and a dicarboxylic acid component comprise an aromatic component) such as a poly(m-phenyleneisophthalamide) together with the aliphatic, alicyclic and/or aromatic polyamide.

5 [0025]

These polyamide components can be used singly or in combination. The preferred polyamide includes at least an aliphatic polyamide.

[0026]

10 The polyamide-series resin having the polyether segment may be used singly or in combination.

[0027]

The number average molecular weight of the polyamide-series resin having a polyether segment is about
15 6,000 to 100,000, preferably about 8,000 to 50,000, and more preferably about 10,000 to 30,000.

[0028]

The proportion of the polyether segment in the polyamide-series resin constituting the resin member may
20 for example be about 10 to 90% by weight, preferably about 20 to 90% by weight, and more preferably about 30 to 90% by weight, relative to the whole resin. Moreover, in the polyamide elastomer, the proportion (weight ratio) of the polyamide segment relative to the polyether segment (e.g.,
25 a PTMG segment) is not particularly limited to a specific one, and for example, may be the former/the latter = about 9/1 to 2/8, preferably about 9/1 to 2.5/7.5, more preferably

about $8/2$ to $3/7$, and particularly about $7/3$ to $4/6$.

[0029]

Moreover, the proportion (weight ratio) of the polyether segment in the polyamide-series resin

5 constituting the resin member, relative to the polyether segment in the thermoplastic polyurethane-series resin constituting the resin member, may be for example about $1/10$ to $10/1$, preferably about $1/8$ to $8/1$, and more preferably about $1/5$ to $5/1$.

10 [0030]

The polyamide-series resin having a polyether segment may have a terminal amino group (a free amino group, $-NH_2$), or may have a terminal carboxyl group. The commercially available polyamide elastomer having a polyether segment
15 usually scarcely has an amino group. Incidentally, the carboxyl group concentration in the polyamide-series resin having a polyether segment is not particularly limited to a specific one, and for example, may be about 0.1 to 200 mmol/kg, preferably about 0.5 to 150 mmol/kg, and more
20 preferably about 1 to 100 mmol/kg.

[0031]

For instance, since the commercially available polyamide elastomer usually scarcely has an amino group, such a polyamide elastomer sometimes insufficiently
25 improves joinability thereof with the thermoplastic polyurethane-series resin. In such a case, joinability between resin members may be enhanced by involving an amino

group- and/or imino group-containing component in at least one of a polyamide-series resin and a thermoplastic polyurethane-series resin each constituting the resin members. Examples of the amino group- and/or imino group-containing component may include another polyamide-series resin (a polyamide-series resin having a terminal amino group, for example, a conventional polyamide-series resin such as the above exemplified aliphatic, alicyclic or aromatic polyamides), an amine compound (e.g., an amine compound having a high amino group concentration and a relatively low molecular weight, such as an amino group-containing polyamide oligomer), and others.

[0032]

As the amine compound, there can be used various amine compounds mixable with a polyamide-series resin having a polyether segment, for example, a polyamine [e.g., a diamine (for example, the above-mentioned aliphatic diamines, alicyclic diamine, and aromatic diamine); in addition a polyamine, for example, an aliphatic polyamine such as a polyalkylenepolyamine such as diethylenetriamine, or triethylenetetramine (e.g., a polyC₂₋₃alkylenepolyamine)], and an amine compound having a relatively low molecular weight (such as a polyamide oligomer). The amine compound can be used singly or in combination. Among these compounds, in terms of joinability, particularly a polyamide oligomer is preferred.

[0033]

As the polyamide oligomer, there may be used a polyamide having a relatively low molecular weight, which is obtained by a conventional manner, for example, by
5 adjusting polycondensation or other conditions and using the above-mentioned polyamide component(s). For example, as a polyamide component to be a raw material, there may be mentioned the combination of the above-mentioned diamine [e.g., an aliphatic diamine (e.g., an alkylenediamine),
10 an alicyclic diamine, and an aromatic diamine] and a dicarboxylic acid (e.g., an aliphatic dicarboxylic acid, and an aromatic dicarboxylic acid), the combination of the above-mentioned diamine and/or dicarboxylic acid and the lactam (e.g., a lactam having about 4 to 20 carbon atoms,
15 such as ω -laurolactam), and other combinations. The polyamide oligomer may be obtained by for example polymerizing the lactam and the aliphatic diamine with heating and stirring under an applied pressure.

[0034]

20 The number average molecular weight of the polyamide oligomer is, for example, about 500 to 10,000, preferably about 500 to 8,000 (e.g., about 1,000 to 7,000), more preferably about 1,000 to 5,000, and usually about 2,000 to 6,000 (e.g., about 3,000 to 6,000). As the polyamide
25 oligomer, for example, the number average molecular weight may be about 1000 to 10,000, preferably about 2,000 to 9,000, and more preferably about 3,000 to 8,000, and use of such

a polyamide oligomer having a relatively high molecular weight improves the joinability (or joining property) of the polyamide-series resin constituting the resin member to the thermoplastic polyurethane.

5 [0035]

Although the polyamide oligomer may be free from a free amino group, the polyamide oligomer usually preferably has a free amino group. When the polyamide oligomer has a free amino group, the polyamide oligomer may have an amino group at least at one terminal of the main chain, may have amino groups at both terminals of the main chain, or may have an amino group at a side chain.

[0036]

The amino group concentration of the amine compound may for example be about 10 to 1000 mmol/kg (preferably about 30 to 700 mmol/kg, and more preferably about 50 to 500 mmol/kg).

[0037]

The proportion of the amine compound (particularly, the polyamide oligomer), relative to 100 parts by weight of the polyamide-series resin having a polyether segment, is, for example, about 0.01 to 10 parts by weight, preferably about 0.1 to 8 parts by weight, and particularly about 0.5 to 7 parts by weight. Excess amount of the amine compound may deteriorate the resin property, particularly in the case of using a polyamide-series resin as a hard resin.

[0038]

The amino group concentration in the polyamide-series resin (or resin composition) constituting the resin member is not particularly limited, and may be, for example, about 0 to 100 mmol/kg, preferably about 0 to 50 mmol/kg, and
5 more preferably about 0 to 30 mmol/kg.

[0039]

In such a range that the effects of the present invention are not deteriorated, the polyamide-series resin member may contain other resins [e.g., a polyester-series
10 resin, a polycarbonate-series resin, a polysulfone-series resin, a polyimide-series resin, a polyketone-series resin, a polyolefinic resin, a styrenic resin, a (meth)acrylic resin, and a halogen-containing vinyl-series resin], and various additives, for example, a filler or reinforcing
15 agent (e.g., a reinforcing fiber), a stabilizer (e.g., a ultraviolet ray absorbing agent, an antioxidant, and a heat stabilizer), a coloring agent, a plasticizer, a lubricant, a flame retardant, an antistatic agent, and others.

[0040]

20 Incidentally, in the case of producing the molded composite article of the present invention, a "warp" in the product sometimes occurs in association with joining due to the difference between mold shrinkage factors of the resin members. In the case where the degree of the
25 correction for the warp is large, there is a possibility that breaking of the joining part or generation of stress crack in each resin member occurs. Therefore, the

polyamide-series resin preferably has lower crystallinity.

[0041]

For example, when the final crystallinity degree of the polyamide block copolymer is adjusted to not more than 40% (e.g., about 5 to 40%), preferably not more than 35% (e.g., about 5 to 35%) and more preferably not more than 30% (e.g., about 10 to 30%), such a copolymer is advantageously used in combination with a thermoplastic polyurethane-series resin member for inhibiting warp generation, and further can provide a flexibility which suits with that of a thermoplastic polyurethane-series resin.

[0042]

Incidentally, the term "the final crystallinity degree" means a degree of crystallinity measured by an X-ray diffraction analysis using a flat plate 1 mm thick, where the flat plate is formed by heating a sample resin to a temperature which is 20°C higher than a melting point thereof, and then cooling the resin to a room temperature at a rate of 3°C/minute by means of a precision (or accurate) heat pressing machine. The melting point of the resin is measured by a differential scanning calorimeter (DSC apparatus) in accordance with JIS K 7122.

[0043]

Incidentally, in a polyamide elastomer which comprises a polyamide homopolymer as a hard segment, the final crystallinity degree can be adjusted by the ratio

of the hard segment and the soft segment.

[0044]

(Polyurethane-series resin)

The thermoplastic polyurethane-series resin
5 constituting the resin member comprises a thermoplastic
polyurethane-series resin having at least a polyether
segment.

[0045]

In the thermoplastic polyurethane-series resin
10 constituting the resin member, the proportion of the
polyether segment relative to the whole thermoplastic
polyurethane-series resin, may for example be about 10 to
90% by weight, preferably about 20 to 90% by weight, and
more preferably about 30 to 90% by weight.

15 [0046]

The thermoplastic polyurethane-series resin having
a polyether segment can be obtained, for example, by reaction
of a diisocyanate with a diol having a polyether unit, if
necessary, with a chain-extension agent.

20 [0047]

The diisocyanate may include an aliphatic
diisocyanate such as hexamethylene diisocyanate (HMDI),
or 2,2,4-trimethylhexamethylene diisocyanate; an
alicyclic diisocyanate such as 1,4-cyclohexane
25 diisocyanate, a dicycloalkylmethane-4,4'-diisocyanate, or
isophorone diisocyanate (IPDI); an aromatic diisocyanate
such as phenylene diisocyanate, tolylene diisocyanate (TDI),

or diphenylmethane-4,4'-diisocyanate (MDI); an
araliphatic diisocyanate such as xylylene diisocyanate;
and others. As the diisocyanate, there may also be used
a compound having an alkyl group (e.g., methyl group)
5 substituted on a main chain or ring thereof. The
diisocyanate(s) may be used singly or in combination.

[0048]

As the diol having a polyether unit, there can be
used a polyether diol [e.g., an aliphatic polyether diol,
10 for example, a poly(oxyC₂₋₄alkylene) glycol such as a
polyethylene glycol, a poly(oxytrimethylene) glycol, a
polypropylene glycol, or a PTMG; a block copolymer of the
poly(oxyalkylene) glycols (e.g., a
polyoxyethylene-polyoxypropylene block copolymer); an
15 aromatic polyether diol, for example, an adduct of an
aromatic diol with an alkylene oxide, such as bisphenol
A-alkylene oxide adduct (e.g., an adduct of a C₂₋₄alkylene
oxide such as ethylene oxide or propylene oxide)]; a
polyester ether diol (e.g., a polyether diol obtained by
20 using a polyester diol (e.g., the below-mentioned polyester
diol) as a part of a diol component), and others. These
diols can be used singly or in combination. Among these
diols, the aliphatic polyether diols such as a polyethylene
glycol and a PTMG are preferred.

25 [0049]

With the diol having a polyether unit, a polyester
diol may be used in combination. The polyester diol may

include a polyester diol (e.g., an aliphatic polyester diol) obtained from a C₄₋₁₂ aliphatic dicarboxylic acid component (e.g., adipic acid), a C₂₋₁₂ aliphatic diol component (e.g., ethylene glycol, propylene glycol, butanediol, and
5 neopentyl glycol), a C₄₋₁₂ lactone component (e.g., ϵ -caprolactone), for example, a poly(ethylene adipate), a poly(1,4-butylene adipate), a poly(1,6-hexane adipate), a poly- ϵ -caprolactone, and others.

[0050]

10 As the chain-extension agent, there may be used a glycol [for example, a short chain glycol, e.g., a C₂₋₁₀ alkylene diol such as ethylene glycol, propylene glycol, 1,4-butanediol, or 1,6-hexanediol; bishydroxyethoxybenzene (BHEB)], and in addition a diamine
15 [for example, an aliphatic diamine such as a C₂₋₁₀ alkylene diamine, e.g., ethylenediamine, trimethylenediamine, tetramethylenediamine, or hexamethylenediamine; an alicyclic diamine such as isophorone diamine; an aromatic diamine such as
20 phenylenediamine, or xylylenediamine]. The chain-extension agent(s) may be used singly or in combination.

[0051]

The thermoplastic polyurethane-series resin may also
25 include a perfect thermoplastic polyurethane obtained by using a diol and a diisocyanate at a substantially equivalent amount, in addition an imperfect thermoplastic

polyisocyanate having a small amount of a residual free (or unreacted) isocyanate, which is obtained by using a slightly excess amount of a diisocyanate relative to a diol.

[0052]

5 Among the thermoplastic polyurethane-series resins, in particular, it is preferred the thermoplastic polyetherurethane elastomer which is obtained by using a diol having a polyether unit, a diisocyanate, and a glycol (e.g., a short chain glycol) as the chain-extension agent.

10 The thermoplastic polyetherurethane elastomer comprises a hard segment (hard block) which is composed of a polyurethane with the use of a glycol and a diisocyanate, and a soft segment (soft block) composed of an aliphatic polyether diol (e.g., a polyethylene glycol and PTMG). The

15 thermoplastic polyurethane-series resin may contain at least a PTMG unit as a polyether segment.

[0053]

These thermoplastic polyurethane-series resins having a polyether segment can be used singly or in

20 combination.

[0054]

As mentioned in the item of the polyamide-series resin, the thermoplastic polyurethane-series resin constituting the resin member may contain the amino group- and/or imino

25 group-containing component (particularly an amine compound such as an amino group-containing polyamide oligomer). The proportion of the amino group- and/or imino group-containing

component (particularly, an amine compound such as an amino group-containing polyamide oligomer) relative to 100 parts by weight of the thermoplastic polyurethane-series resin having a polyether segment, is, for example, about 0.01 to 10 parts by weight, preferably about 0.1 to 8 parts by weight, and particularly about 0.5 to 7 parts by weight.

[0055]

In such a range that the effects of the present invention are not deteriorated, the thermoplastic polyurethane-series resin member may comprise other resin(s) (e.g., a thermoplastic resin, particularly a thermoplastic elastomer such as a polyamide-series elastomer, a polyester-series elastomer, or a polyolefinic elastomer), a stabilizer (e.g., a heat stabilizer, an ultraviolet ray absorbing agent, an antioxidant), a plasticizer, a lubricant, a filler, a coloring agent, a flame retardant, an antistatic agent, and others.

[0056]

Since both polyamide-series resin and thermoplastic polyurethane-series resin have a polyether segment in the molded composite article of the present invention, and since the affinity between both resins is high, the polyamide-series resin and the thermoplastic polyurethane-series resin are firmly joined together without an adhesive. The bonded strength or joined strength is usually not less than 30 N/cm, and cohesive failure sometimes occurs along with separation of the

polyamide-series resin member (e.g., a hard resin member)
from the thermoplastic polyurethane-series resin member
(e.g., a soft resin member). The bonded strength of such
a molded composite article is usually 30 N/cm to cohesive
5 failure, preferably not less than 40 N/cm, and particularly
not less than 50 N/cm (not less than 50 N/cm to cohesive
failure).

[0057]

[Production process of molded composite article]

10 The molded composite article of the present invention
may be produced by joining the polyamide-series resin with
the thermoplastic polyurethane-series resin under heating.
The joining may be usually ensured by heating at least one
resin selected from the polyamide-series resin and the
15 thermoplastic polyurethane-series resin to be molten, and
bringing one resin in the molten state into contact with
the other resin. Such a molded composite article may be
produced by joining the polyamide-series resin with the
thermoplastic polyurethane-series resin in a molding
20 process by means of a conventional molding method such as
a thermoforming (e.g., a heat press molding, an injection
press molding), an injection molding (e.g., an insert
injection molding, a two-color (or double) injection molding,
a core-back injection molding, a sandwich injection molding),
25 an extrusion molding (e.g., a co-extrusion molding, a T-die
lamination molding), or a blow molding.

[0058]

For example, in a molding method such as an insert injection molding or an injection press molding, the both resins may be joined together by heating and melting the thermoplastic polyurethane-series resin, and molding the thermoplastic polyurethane-series resin in a molten state with contacting with at least a part of a resin member composed of the polyamide-series resin. The both resins may also be joined together by heating the polyamide-series resin to be molten, and bringing the polyamide-series resin in the molten state into contact with at least a part of a resin member composed of the thermoplastic polyurethane-series resin. Moreover, in a molding method such as a double injection molding or a co-extrusion molding, joining of the both resins may be ensured by heating and melting both the polyamide-series resin and the thermoplastic polyurethane-series resin differently, and molding the molten polyamide-series resin and the molten thermoplastic polyurethane-series resin with contacting with each other. A molded composite article in which the polyamide-series resin member is firmly joined to the polyurethane-series resin member can be obtained by melting at least one resin selected from the polyamide-series resin and the polyurethane-series resin, bringing the polyamide-series resin into contact with the thermoplastic polyurethane-series resin for joining, and usually cooling the resulting matter. Moreover, depending on a purpose and an application, it is sufficient to join the

polyamide-series resin member to the thermoplastic
polyurethane-series resin member at least in part.

[0059]

Incidentally, the resin can be molten by heating to
5 a temperature of not less than a melting point thereof.
In the case of a substantially uncrystallized resin, the
resin can be molten by heating to a temperature of not less
than a glass transition point (Tg) thereof.

[0060]

10 According to the present invention, since each of
the polyamide-series resin and the thermoplastic
polyurethane-series resin has a polyether segment, high
affinity between both resins drastically improves bonded
strength between resin members even in the molded composite
15 article using different materials.

[0061]

As described above, it is not particularly limited
which of the resins between the polyamide-series resin and
the polyurethane-series resin is molten. A soft resin (the
20 polyurethane-series resin) having a usually lower melting
point or glass transition point (Tg) may be heated, and
may be joined to a hard resin member comprising a hard resin
(the polyamide-series resin) having a higher melting point
or Tg. Moreover, a hard resin (the polyamide-series resin)
25 having a generally higher melting point or Tg may be heated,
and may be joined to a soft resin member comprising a soft
resin (the polyurethane-series resin) having a lower melting

point or Tg.

[0062]

Among these methods, in particular, the former method has an advantage over conventional techniques since the effects of the present invention are characteristically and effectively exhibited. In the conventional method using simple physical thermal fusing, when letting a precedently molded polyamide-series resin member joined with a followingly molding polyurethane-series resin, the molding temperature of the polyurethane-series resin becomes lower than the melting point of the precedently molded polyamide-series resin in many cases, and therefore thermal fusing is difficult to proceed. Moreover, even when the molding temperature of the polyurethane-series resin is higher than the melting point of the polyamide-series resin, the heat quantity is often insufficient to melt the surface of the polyamide-series resin member. Therefore, the conventional techniques usually never comprise such a manner as molding the polyamide-series resin member before molding the polyurethane-series resin. However, according to the present invention, even in such a case, the polyamide-series resin member and the thermoplastic polyurethane-series resin can be more easily joined together by an action of the polyether segments contained in the polyamide-series resin and the thermoplastic polyurethane-series resin. Accordingly, the present invention can increase the freedom of the production process

of the composite article and can also rationalize the process step to a large degree.

[0063]

According to the present invention, although the hard
5 resin usually comprises the polyamide-series resin and the
soft resin usually comprises the thermoplastic
polyurethane-series resin in practical cases, the hard resin
may comprise the thermoplastic polyurethane-series resin
and the soft resin may comprise the polyamide-series resin.
10 Moreover, the hardness of the polyamide-series resin may
be the same level as that of the thermoplastic
polyurethane-series resin.

[0064]

To be more precise, in the heat press molding, a molded
15 composite article may be produced by melting at least one
resin of the hard resin (or composition) and the soft resin
(or composition) in a metal mold of the press molding,
bringing the both resins into contact with each other under
an applied pressure, and joining the resins to each other.
20 In the heat press molding, the hard resin and/or the soft
resin may be filled in the metal mold in a pellet form,
a powdered form or other form(s), or may be loaded to the
metal mold as a molded article precedently formed by other
molding method.

25 [0065]

In the insert injection molding, a molded composite
article may be produced by molding any one of the hard resin

(or resin composition) or the soft resin (or resin composition) with the use of a molding method (such as an injection molding, an extrusion molding, a sheet molding, or a film molding), inserting or putting thus shaped molded
5 article in a metal mold, and then injecting the other resin to the space or cavity between the molded article and the metal mold. In the insert injection molding, the molded article to be inserted in the metal mold is preferably pre-heated.

10 [0066]

In the two-color (or double) injection molding, a molded composite article may be produced by injecting any one component of the hard resin (or resin composition) or the soft resin (or resin composition) to a metal mold by
15 means of two injection molding machines or more, and exchanging cavity of the metal mold by rotation or movement of the metal mold, and injecting the other component to the space or cavity between thus obtained molded article and the metal mold.

20 [0067]

In the core-back injection molding, a molded composite article may be produced by injecting any one component of the hard resin (or resin composition) or the soft resin (or resin composition) in a metal mold, enlarging the cavity
25 of the metal mold, and injecting the other component to the space or cavity between thus obtained molded article and the metal mold.

[0068]

Among these molding methods, particularly from the viewpoint of mass production or other properties, suitable methods are, for example, the heat press molding such as
5 injection press molding, and the injection molding (e.g., insert injection molding, double injection molding, core-back injection molding, sandwich injection molding).

[0069]

In the thermal fusing, the melting temperature (or
10 thermal fusing temperature) of the hard resin and/or soft resin may be selected depending on the species of the both resins (or resin compositions). For example, in the heat press molding, the melting temperature may be about 100 to 250°C, preferably about 120 to 230°C, and more preferably
15 about 150 to 220°C. Moreover, in the injection molding, the temperature of the resin in the molding cylinder may for example be about 200 to 300°C, preferably about 220 to 280°C, and more preferably about 240 to 280°C.

[0070]

20 The structure and configuration of the molded composite article is not particularly limited to a specific one, and may be a structure suitable for design, decorative property, touch or others. For example, such a structure may be obtained by coating or laminating a part or all of
25 the soft resin member with the hard resin member, and usually, preferably obtained by coating or laminating a part or all of the hard resin member with the soft resin member (for

example, obtained by coating part of the hard resin member, which contacts with human body (such as a hand), with the soft resin member). Moreover, the concrete structure includes, for example, a two-dimensional structure (such as a sheet-like form, or a plate-like form), and a
5 three-dimensional structure (such as a stick-like form, a tube-like form, a casing, or a housing).

[0071]

According to the present invention, the hard resin
10 and the soft resin can be directly and firmly joined together by thermal fusing without (going through) complicated production steps (e.g., a step for creating a concavo-convex site in the composite area, a step for coating an adhesive). Therefore, the present invention ensures to obtain a
15 lightweight and strong molded composite article improved in properties such as design, decorative property, or good touch or texture (e.g., soft texture, flexibility).

[Industrial Applicability]

[0072]

20 The molded composite article of the present invention may be used as various industrial components (or parts), for example, an automotive part (e.g., an automotive interior part such as an instrument panel, a center panel, a center console box, a door trim, a pillar, an assist grip,
25 a steering wheel, or an air bag cover; an automotive exterior part such as a fender, or a bumper; and an automotive functional component such as a rack and pinion boot, a

suspension boot, or a constant velocity joint boot), a household electrical part (e.g., a cleaner bumper, a switch of a remote control, and a key top of office automation (OA) apparatus), a product to be used in water (e.g., swimming
5 goggles, and a cover of a underwater camera), an industrial part (a cover part; various industrial parts equipped with a packing for the purpose of sealing property, water proofing property, sound insulating property, vibration insulating property, or other properties; and an industrial rubber
10 roller), an electric or electronic device part (e.g., a curl cord wire covering, a belt, a hose, a tube, and a sound deadening gear), sports goods, shoes goods (e.g., athletic shoes, a shoe sole), and a part requiring design or decorative property (e.g., dark glasses and glasses).

15 [0073]

Among them, the molded composite article is particularly suitable for a constitutive member of the shoe or the roll (e.g., a rubber roller). The constitutive member of the shoe includes a shoe part such as a shoe sole (sole),
20 or a shoe upper, and others. Moreover, the molded composite article may form (or constitute) athletic shoes, work shoes (e.g., boots, rain shoes, shoes for gardening). In such a shoe application, since a combination of a hard or glass fiber-reinforced polyamide-series resin and a soft
25 polyurethane-series resin, which was difficult in the past, becomes easy, it is, for example, possible to compound different grades of materials in many layers. Accordingly,

the molded composite article greatly contributes to improvement in design or functionality of the shoe.

[0074]

Further, in the roll (e.g., a rubber roller)
5 application, for example, the roll may comprise an axis
(shaft) in which at least the surface layer comprises a
polyamide-series resin, and a thermoplastic
polyurethane-series resin layer formed along the
surrounding surface of the axis. The axis may be obtained
10 by forming a polyamide-series resin layer on the surface
of the metal shaft, or may be an axis comprising a
polyamide-series resin. In such a roller application,
since a cutting finish for obtaining a shaft precision and
a surface finish of a thermoplastic polyurethane-series
15 resin can be conducted in one operation by the same grinding
machine, the production process of the roller can be
significantly abbreviated and the cost can be exponentially
reduced. Moreover, since such a roller given by chemically
joining has high bonded strength and merely has the space
20 or cavity between the axis and the roll, the roller can
tolerate the usage in a high torque.

[Examples]

[0075]

The following examples are intended to describe this
25 invention in further detail and should by no means be
interpreted as defining the scope of the invention.

[0076]

(Evaluation of thermal fusing)

The molded composite articles obtained in Examples and Comparative Examples were cut into a size of 20 mm in width and 100 mm in length. In each cut piece, the tensile
5 test was conducted by drawing a tong hold to 180° direction at a drawn speed of 20 mm/minute. Through the tensile test, the peel strength in the fusing interfaces between a hard resin member and a soft resin member was measured. On the basis of the peel strength, the thermal fusing property
10 between the hard resin member and the soft resin member was evaluated.

[0077]

Examples 1 to 8 and Comparative Examples 1 to 2

A molded article (flat plate having 100 mm width,
15 100 mm long and 2 mm thick) was formed by injection molding with the polyamide elastomers or polyamides, and the surface of about one-fourth in the above molded article was covered with an aluminum foil. Subsequently, a covered resin member was placed in a flat plate metal mold having 100 mm width,
20 100 mm long and 4 mm depth, and the thermoplastic polyurethane (TPU) was injection-molded into the void of the metal mold to give a molded composite article. The injection molding of the TPU was conducted at a cylinder temperature of 205°C and a metal mold temperature of 60°C.

25 [0078]

Incidentally, a polyether-series thermoplastic polyurethane C1 (Erastollan, ET890, manufactured by BASF)

or a polyether-series thermoplastic polyurethane C2 (Erastollan, 1195ATR, manufactured by BASF) was used as the above TPU.

[0079]

5 Polyamide elastomers or a polyamide to be used were prepared in the following procedure.

[0080]

(1) Polyamide elastomer (A1)

Lauryllactam (500 g) and dodecanedioic acid (50 g)
10 were added into a pressure vessel, and stirred at 270°C and
20 atmospheres for 3 hours under nitrogen gas flow. A
polytetramethylene glycol (which has a molecular weight
of 1300 and hydroxyl groups as both ends) (500 g) was added
to thus obtained mixture, and stirred for 5 hours with heating
15 under a reduced pressure to obtain a polyamide elastomer
(A1).

[0081]

(2) Polyamide elastomer (A2)

A polyamide elastomer (A2) was prepared in the same
20 manner with the above (A1) except that lauryllactam (800
g), dodecanedioic acid (90 g) and a polytetramethylene
glycol (320 g) were used.

[0082]

(3) Polyamide elastomer (A3)

25 A polyamide elastomer (A3) was prepared in the same
manner with the above (A1) except that lauryllactam (300
g) and dodecanedioic acid (30 g) and a polytetramethylene

glycol (450 g) were used.

[0083]

(4) Polyamide elastomer (A4)

A polyamide elastomer (A4) was prepared in the same
5 manner with the above (A1) except that lauryllactam (500
g) and dodecanedioic acid (25 g) were used, and that a
polypropylene glycol (which has a molecular weight of 1000
and hydroxyl groups as both ends) (500g) was used instead
of the polytetramethylene glycol.

10 [0084]

(5) Polyamide elastomer (A5)

A polyamide elastomer (A5) was prepared in the same
manner with the above (A4) except that a polyethylene glycol
(which has a molecular weight of 2000 and hydroxyl groups
15 as both ends) (500 g) was used instead of the polypropylene
glycol.

[0085]

(6) Polyamide (B1)

Lauryllactam (1000 g) and dodecanedioic acid (110
20 g) were heated to 250 to 260°C in the presence of a small
amount of phosphoric acid in an autoclave substituted with
nitrogen gas, followed by water in the system together with
nitrogen gas to discharge out of the system over 4 hours.
Subsequently, the temperature of the system was gradually
25 increased up to 275°C over 1 hour, and residual water was
removed to outside of the system. Thereafter, the system
was cooled to give a comparative polyamide (B1).

[0086]

The molded composite articles of Examples and Comparative Examples were examined for the peel strength, and the results are shown in Table 1.

5 [0087]

[Table 1]

Table 1

	Polyamide elastomer	Polyurethane	Peel strength N/cm
Example 1	A1	C1	140
Example 2	A2	C1	90
Example 3	A3	C1	180
Example 4	A4	C1	130
Example 5	A5	C1	130
Example 6	A1	C2	140
Example 7	A2	C2	100
Example 8	A5	C2	140
Comparative Example 1	B1	C1	16
Comparative Example 2	B1	C2	10

[Document Name] Abstract

[Abstract]

[Object(s)] To achieve a direct and firm bonding between
a polyamide-series resin member and a thermoplastic
5 polyurethane-series resin member which were different in
properties from each other by a simple process.

[Means to Solve the Problems] A molded composite article
comprises a resin member comprising a polyamide-series resin
and a resin member comprising a thermoplastic
10 polyurethane-series resin, and these members are directly
joined with each other; and each of the polyamide-series
resin and the thermoplastic polyurethane-series resin has
a polyether segment. The molded composite article can be
produced by heating at least one of the polyamide-series
15 resin and the thermoplastic polyurethane-series resin to
join these resins with each other.

[Selected Fig.] none

Applicant Record

Identification No. [000108982]

1. Date of Alternation July 12, 2001

[Reason of Alternation] change of name

Address 2-5, Kasumigaseki 3-chome,
Chiyoda-ku, Tokyo

Name Daicel-Degussa, Ltd.

2. Date of Alternation May 11, 2004

[Reason of Alternation] change of address

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